Status of Water Pollution Control in the Ontario Oil Refining Industry

O.W.R.C.
~~Industrial~~
~~Wastes~~
Report

Ontario
Water Resources
Commission

135 St. Clair Ave. W.
Toronto 195, Ontario

A REPORT ON THE
STATUS OF WATER POLLUTION CONTROL IN THE
ONTARIO OIL REFINING INDUSTRY

by

Division of Industrial Wastes

ONTARIO WATER RESOURCES COMMISSION

TABLE OF CONTENTS

INTRODUCTION

During the summer of 1968, intensive industrial waste surveys were carried out at all of the seven Ontario oil refineries. These surveys involved the collection and analysis of effluent samples over at least a twenty-four hour operating period and, where possible, the collection of samples of in-plant waste sources.

The purpose of these intensive surveys was to provide comparative data for an appraisal of the overall status of water pollution control in the Ontario oil refining industry.

It is hoped that the data compiled in this report will provide a basis for future policy in the OWRC regulatory control programme for the oil industry.

SUMMARY

The status of water pollution control in the Ontario oil refining industry is generally satisfactory. Other industries such as the steel and organic chemicals manufacturing industries are substantially greater sources of the oil and phenolic pollutants commonly associated with oil refining wastewaters.

The total daily waste loadings from the Ontario oil refining industry in terms of phenolics, non-volatile oil, COD, and total kjeldahl nitrogen were found to be approximately 220 lbs., 9,050 lb., 71,500 lbs., and 30,400 lbs. respectively in a total waste flow of 180 mgd.

The larger, older and more complex refineries account for 73 per cent of the phenolic and 70 per cent of the non-volatile oil waste loadings while having only 44 per cent of the total crude oil refining capacity.

The Ontario industry is generally superior to the United States oil refining industry in terms of waste loadings per unit of production for similar refineries. Waste loadings for the Ontario refineries in terms of non-volatile oils and phenolics as related to crude oil processed, vary between 0.002 and 1.94 lbs. phenolics and 0 to 44.5 lbs. non-volatile oil per thousand barrels of crude oil processed.

In general, the pollution problems associated with the Ontario oil industry are mainly related to inadequate control of accidental losses of high strength wastes. These problems have been identified in the individual refinery reports and drawn to the attention of management. In all cases, positive action is planned or has been implemented to deal with these situations.

A number of recommendations have been made to improve the OWRC regulatory programme for the oil industry in the area of effluent quality objectives, stream assimilation studies and contingency planning to deal with oil spills.

It is also recommended that the Ontario oil industry intensify its efforts to control and deal with accidental losses of high strength wastes.

HISTORY OF THE OIL INDUSTRY IN ONTARIO

The oil industry in Ontario began with the sinking of North America's first commercial oil well by James Miller Williams at Oil Springs in Lambton County in 1858. Prior to this, the medicinal properties of asphaltic gums found in the marshy areas of Enniskillen Township had been known to the Indians and the commercial exploitation of these deposits by Charles N. Tripp pre-dates the William oil well by at least six years. While petroleum had been known and used by man since the beginning of civilization, credit for first recovering and manufacturing a marketable product from oil in Canada must therefore go to Charles N. Tripp.

It is doubtful whether serious consideration was given to pollution control during these early days of the oil industry.

In 1862 the first case of major oil pollution of an Ontario stream arising from the oil industry occurred when the Shaw gusher at Oil Springs deposited 3000 barrels of oil daily into Black Creek during a one week period until it was capped, and which eventually coated the distant waters of Lake St. Clair with a black film. The discovery of the Shaw gusher was the prelude to the drilling of numerous other flowing wells, which overtaxed the limited storage capacity available at that time and contemporary accounts indicate that during the spring and summer of 1862, no less than 5 million barrels of oil floated off upon the waters of Black Creek. The surface of

Black Creek was a foot deep in oil and 40 to 50 acres in the vicinity of the wells were covered to a depth of one to three feet.

The first oil refineries were built close to the sources of crude oil in Oil Springs and Petrolia and were usually owned and operated by the producers. In 1864, it is reported that there were seven oil refineries in Petrolia and twenty in Oil Springs with a combined capacity of 500 barrels per day. Refining in those days was carried out in primitive cast iron stills shaped like ink bottles with condenser tubes emerging from the top. London and Hamilton, were also important early centres of the oil refining industry and after 1870, Sarnia began to assume increasing prominence. Transportation problems, the depletion of Oil Springs reserves, increasing demand and the need to import crude oil from the United States, all tended to encourage the development of Sarnia as an oil refining centre. The first refinery in Sarnia was built in 1871 and the Imperial Oil Company transferred its refining operations to Sarnia in 1897. Nevertheless, in the 1880's Petrolia could boast the largest oil refinery in Canada -- that of J. L. Englehart and Company and this subsequently formed the basis of the Imperial Oil Company refining operations which were eventually transferred to Sarnia.

Imperial Oil continued to be the dominant industry in Sarnia, right up to the development of the area as a war time petrochemical and rubber manufacturing centre. Post war competition in basic oil refining was not provided to Imperial Oil in the area until the advent of The Canadian Oil Company Limited (subsequently Shell Canada Limited) and Sun Oil Company Limited refineries in the early 1950's.

The development of the western shore of Lake Ontario as a major oil refining centre began at a much later date than the Sarnia-Petrolia region and parallelled the growth of the Toronto-Hamilton area as a major urban and industrial-region, and therefore a major market for petroleum products. The forerunner of the existing Regent Refining Company Limited refinery was built in Port Credit in the 1920's.

The present Gulf Oil Canada Limited refinery began operations in the 1940's producing much needed aviation gasolines and lubricants for the war effort.

These two refineries were initially dependent upon imported crude oil, and these foreign crude oil sources were subsequently augmented and then replaced by western Canadian crude oil brought in by pipe-line.

The availability of unlimited quantities of crude oil by pipe-line and the rapidly expanding Toronto-Hamilton market were probably major factors in the construction of the two newer refineries in Oakville, namely, that of B. P. Canada Limited, under the auspices of Cities Service Canada Limited in 1960 and the Shell Canada Limited refinery in 1963.

In terms of pollution control technology, the newer refineries tended to be more advanced. Since the advent of the OWRC, and in many cases prior to this, the industry as a whole has made significant progress in pollution control and at the present time, the level of technology and the degree of pollution control efficiency in this industry are both very high.

POLLUTION PROBLEMS ASSOCIATED WITH THE OIL INDUSTRY

Major disasters such as the wreck of The Torrey Canyon and the leaking offshore oil well in Southern California have focussed public attention on the pollution potential of the oil industry. Apart from the aesthetic consequences and potential fire hazards, major losses of oil tend to adversely affect the aquatic environment in a number of ways:

1. The inhibition of the natural atmospheric reaeration of a watercourse by the coating of oil on the surface.

2. The introduction of soluble organic matter into the watercourse which may be toxic to aquatic life and/or deplete the dissolved oxygen of the watercourse by biochemical oxidation.

3. The introduction of objectionable tastes and odours to the watercourse.

4. The destruction of aquatic plants and animals generally.

All of these factors tend to reduce the availability of the watercourse for recreational, domestic, agricultural or industrial uses.

Fortunately, surface waters in Ontario are seldom exposed to the massive oil spills envisaged in the foregoing. Nevertheless, the cumulative effects of low level continuous oil losses and/or spills of small quantities of oil are in some respects similar to the effects of major oil spills. The oil coated shoreline of the St. Clair River at certain locations and the banks of the Talford Creek in the Sarnia area bear witness to this fact.

The effects of chemical losses, including dissolved organic materials, are less obvious and more difficult to assess. Much attention has been placed on the presence of phenolics in refinery wastewaters and their effects on the potability of domestic water supplies. Less clear are the effects of dissolved hydrocarbons, sulphides, cyanides and other chemical waste constituents. Dissolved hydrocarbons, particularly aromatics, are liable to be toxic to aquatic life and resistent to biochemical decay and thus, the effects could be quite long term.

Sulphides and cyanides are toxic and objectionable waste constituents but they tend to be oxidized in the receiving stream by chemical or biochemical processes.

SOURCES OF LIQUID WASTES IN AN OIL REFINERY

The predominant wastewater from most oil refining operations is cooling water. This can be once-through cooling water from heat exchangers and condensers, oil contaminated cooling water from vacuum ejector systems or blowdown from recirculating cooling systems with a high dissolved solids content. Clean once-through cooling water can be further sub-divided into non-oily and potentially oily depending upon the nature of the product stream being cooled. Cooling waters from volatile products systems are considered non-oily since in the event of a leak in the system, the product tends to vapourize. The converse applies to cooling waters from non-volatile products systems. Clean cooling waters can also be differentiated into potentially oily and non-oily by the pressure differential on the material of construction between the product and the cooling water sides in the exchanger or condenser. High product

pressure would tend to increase the possibility of oil contaminated cooling water in the event of a leak in the system.

As mentioned previously, oily process waters may arise from vacuum ejector systems cooling water. Condensates from steam stripping operations and water present in feed streams also give rise to oily process wastewaters, but these are considered under sour waters, since they are generally rich in sulphides and, in some cases, phenolics. Oily wastewaters also arise from tank bottom drainage, pump glands, and pad drainage, marine ballast, crude oil desalters and tank farm drainage.

Sour waters or foul condensates originate mainly in crude distillation and cracking operations. These may contain significant concentrations of sulphides, ammonia (introduced as a corrosion control measure in overhead accumulators or produced in hydrogen treating units) and phenolics. Phenolic foul condensates are mainly derived from cracking operations.

Chemical wastes such as spent caustic and acids generally originate from secondary product treating operations such as sweetening, caustic treating and additive treating and also from catalytic processes such as cracking, alkylation, polymerization and isomerization.

WASTE TREATMENT AND DISPOSAL

Waste treatment and disposal technology in the oil industry encompasses a wide variety of physical, chemical and biological processes. These range from simple gravity separation to complex chemical treatment, bio-oxidation and chemical oxidation systems. Certain fundamental processes such as gravity separation are common to all Ontario oil refineries whereas other processes such as deep well injection are confined to to specific refineries or areas.

Gravity separation for the removal of floating and settleable suspended solids is usually carried out in rectangular tanks conforming to American Petroleum Institute specifications.

Exceptions to this are the Shell Canada Limited and Imperial Oil Enterprises refineries in Sarnia. The Sarnia refinery of Shell Canada Limited utilizes circular gravity

oil separators and the Imperial Oil Enterprises refinery uses both circular oil separators and A. P. I. rectangular separators.

The effectiveness of gravity separation is usually dependent upon a number of factors:

1. Even, non-turbulent flow distribution to the separator.

2. A residence time compatible with the susceptibility of the oil and suspended solids in the wastewater to gravity separation which is further related to the density and size of the oil globules and the amount and characteristics of the suspended solids.

3. Proper operation of the separator, involving regular withdrawal of accumulated oil and suspended matter and the maintenance of the facilities in a good state of repair.

The segregation of wastewaters into various waste streams according to the characteristics of the wastewater is practiced to varying degrees by all of the Ontario oil refineries. The newer refineries are, predictably, more advanced in this area and generally have individual sewers or waste handling systems dealing with cooling waters, potentially oily wastewaters, oily process wastes, phenolic wastes, storm drainage, marine ballast water and chemical wastes, as well as facilities for handling sludges and spent acids and alkalies. Obviously, maximum waste segregation is essential to economical and reliable waste treatment. Most Ontario refineries segregate phenolic foul condensates and spent caustics from main sewer systems for separate treatment and/or disposal, while the separate disposal of major cooling water waste flows is practised to varying degrees by most refineries. In general, the main waste segregation problems are associated with the incomplete separation of clean cooling waters from oily waste flows with its consequent wasteful utilization of separator capacity, the disposal of storm drainage in conjunction with process wastes, the disposal of emulsified oily wastewaters or high phenolic oily waste streams to gravity separation treatment systems and, finally, the lack of emergency holding facilities for accidental spills and other irregular discharges of high strength wastes.

Biological treatment facilities for high phenolic waste streams are largely based on the activated sludge process. The B.P. Canada Limited refinery in Oakville also uses trickling filters as a roughing pretreatment prior to activated sludge treatment, while the Shell Canada Limited refinery in Sarnia is dependent upon deep well injection as an alternative to biological treatment. The Sun Oil Company Limited utilizes deep well injection for high phenolic wastes while low phenolic wastes are biologically treated.

Process wastes directed to biological treatment facilities fall into two general categories as follows:

a) Sour water stripper effluent and similar high phenolic waste streams.

b) The total process waste flow, including cooling tower blow-down but exclusive of strong spent acids and alkalies, from those refineries with recirculating cooling water systems.

Steam stripping of foul condensates, (sour waters) to remove hydrogen sulphide and sometimes ammonia is an essential precursor to biological treatment of these wastewaters. There are numerous stripper designs, but most are based on the passage of sour wastes down a trayed or packed tower countercurrent to the stripping steam. Higher operating temperatures and stripping rates are required to remove ammonia as well as hydrogen sulphide and where subsequent biological treatment processes are not adversely affected by the effluent ammonia content, strippers are generally operated to remove mainly hydrogen sulphide. Stripping with flue gas is practiced at the Imperial Oil Enterprises Limited and Sun Oil Company Limited refineries and this process removes exclusively hydrogen sulphide.

Chemical treatment is practised at only two refineries, namely the Oakville refineries of B.P. Canada Limited and Shell Canada Limited. In the latter refinery, this involves chlorination of the final plant effluent while the B.P. Canada Limited refinery uses chemical flocculating agents and coagulant aids to achieve better primary gravity separation and ozone as a final treatment for chemical oxidation after biological treatment and prior to sand filtration. Facilities are also available at this refinery for activated carbon treatment.

The treatment and disposal of spent acids, alkalies and sludges varies from refinery to refinery. Contract disposal

of many of these wastes is practised at most refineries and this has caused the development of a centralized industrial waste disposal facility at Sarnia, involving incineration of solid and liquid wastes, land disposal and deep well injection. Some strong spent chemical wastes in the Sarnia refineries are disposed by deep well injection within the refinery property. Weak spent caustics are either disposed by deep well injection or directed to biological treatment facilities (The Texaco Canada Limited Refinery utilizes flue gas neutralization of weak spent caustic prior to disposal to biological treatment facilities) while strong phenolic spent caustics are sold to chemical processing companies for recovery of phenolics and other organic chemicals.

CONDUCT OF SURVEY

During the summer of 1968, intensive industrial waste surveys were conducted at all the seven oil refineries in Ontario. These surveys attempted to define the nature, sources and disposal of all refinery wastewaters and to provide detailed chemical analytical data on in-plant wastewaters and the final effluents.

Prior to these surveys, a questionnaire was sent to all refineries requesting detailed information on all refinery wastes. The replies were subsequently used as a basis for discussion during the pre-survey meetings with refinery technical personnel. Based on the information obtained from the questionnaire and the pre-survey discussions, the scope and intensity of each individual refinery survey was determined.

Sampling

In order to determine variations in effluent characteristics during a working day, composite effluent samples over a twenty-four hour period were obtained at all of the refineries and in some cases, this period was extended to forty-eight hours. The samples, in most cases, involved the collection of equal aliquots of the effluents at regular and frequent intervals during an eight-hour period and combination of these aliquote to obtain a composite sample representative of the eight-hour period. In some cases, eight-hour composites were obtained from company automatic samplers, but in order to maintain consistency in sampling, the samplers were operated manually to obtain the sample. Three eight-hour composites were obtained for each twenty-four hour period and submitted separately for analysis.

Where possible and practicable, samples of in-plant waste sources were also taken. In some cases, it was only possible to obtain grab samples, or a series of grab samples of these waste sources and in other cases, composite samples, involving more frequent grab sampling, were obtained. This is largely the area where the intensity and scope of the individual refinery surveys varied. In some refineries, in-plant waste sources were accessible and freely available for sampling, while in others, they were not.

In general, the analysis of effluent and in-plant waste samples was the same, and common procedures were developed for the preservation of samples for analysis for parameters which were known to be affected by the time delay involved in shipping samples to the OWRC Laboratory in Toronto. In this regard, samples for phenols, cyanides and sulphides analysis were preserved with acidified copper sulphate, sodium hydroxide and zinc acetate solutions respectively.

Duplicate samples were taken at all locations for ether solubles, phenols, cyanides and sulphides analysis, since these analyses either required preservatives or a separate sample bottle.

ANALYTICAL PROCEDURES

In general, the analysis methods used in OWRC Laboratories conform to the procedures described in "Standard Methods for the Examination of Water and Wastewater," 12th edition, published by the U.S. Public Health Association. However, in many cases, minor modifications, and in some cases major revisions, of these methods are practiced at OWRC Laboratories, usually in the interests of speed and accuracy or to accomodate the use of instrumented analytical techniques.

Much discussion has been, and continues to be centred around the accuracy and interpretation of phenols determinations. Part of the problem appears to stem from the fact that phenol is a generic rather than a specific term. There are many phenolic compounds capable of reacting to varying degrees with the reagents used in the standard analytical procedures. It is these variations in the nature of the phenolic material and the degree of reaction in the analysis method which makes the quantitative interpretation of the results difficult. The interpretation is further complicated by the fact that the principal effect of phenolics in natural water is largely qualitative, that is, the imparting of an objectionable taste to the water. A quantitative relationship has been established between the concentration of specific phenols in water and the threshold taste and odour of the water, but correlation

between this and the effects of mixed phenolic industrial wastes is not clear.

Interference is also a significant factor in the phenols analysis. Both the Gibbs procedure and the 4-amino-antipyrene method are dependent upon a coupling reaction between the reagent and the phenolic compound in the para-position of the phenolic ring. High molecular weight compounds other than phenolics which possess mobile hydrogen atoms will also undergo this reaction and give rise to positive interference in the analysis. In this category are compounds such as amines and fatty acids. Negative interference may result from the presence of stable substituents in the para-position of the phenolic ring or from the presence of oxidizing and reducing agents or excessive acidity, all of which influence the conditions for the coupling reaction.

The oil content of wastewaters as determined by the ether solubles analysis is essentially indicative of ether soluble non-volatile oils, since the evaporation stage of the determination would tend to vapourize volatile oils with the ether solvent. Also, in cases where oil is present which is partially volatile at the evaporation temperature, it becomes difficult to evaporate to constant weight and consequently the accuracy of the measurement is imprecise. In relating ether solubles analysis to conditions in the receiving stream, it may be justifiable to assume that the effects of the volatile oil portion not determined by the test are not significant in the stream since this portion would tend to be driven off to the atmosphere during passage in the stream. However, temperature conditions in the receiving stream are unlikely to approach that of the ether solubles test, and although turbulence,residence time and partial pressure are also factors in the volatility of hydrocarbons in the receiving stream, the effects of volatile oils on the stream are likely to be significant.

Also, in the category of volatile oils are hydrocarbons such as benzene and toluene which are, to a significant degree, soluble in water and are toxic. Such compounds are not determined in the ether solubles analysis, although they may contribute to the COD and BOD of the wastewater. The extent of this contribution is unknown and impossible to relate to the toxicity effects attributable to these compounds which may be encountered in the receiving watercourse.

DISCUSSION OF FINDINGS

Classification of Refineries

Because of the limited number of oil refineries on which

this survey is based, it is difficult, if not impossible, to make rigorous comparisons between the various refineries or to draw precise comclusions with respect to unit waste loadings from specific production units. It is known, for example, that catalytic cracking operations are the predominant source of phenolics in refinery wastewaters, yet the variation and complexity of these operations and the lack of adequate analytical data from this survey make it impossible to determine the amount of phenolics produced per unit of throughput. Furthermore, the variation in the nature of the oil refineries in Ontario makes the interpretation of an overall comparison of such data for these refineries questionable. It is, for example, doubtful whether a meaningful comparison can be made in terms of pollution control between a large integrated oil refining and petrochemical processing complex such as Imperial Oil Enterprises Limited and a relatively small and simple oil refining operation such as the Sarnia refinery of Sun Oil Company Limited. It is for this reason that some method of grading the seven Ontario oil refineries in terms of size, age, complexity and level of technology (including pollution control technology) was sought. Using the U.S. Department of the Interior, F.W.P.C.A. Cost of Clean Water, Volume III Industrial Waste Profile No. 5 as a guide, the relative levels of technology and the nature of the production units associated with these levels of technology are as indicated in the following summary:

RELATIVE LEVELS OF REFINING TECHNOLOGY AND ASSOCIATED PRODUCTION UNITS

	Older Technology	Typical Technology	New Technology
a)	Crude Oil Storage	Crude Oil Storage	Crude Oil Storage
b)	Chemical Desalting	Electrostatic Desalting	Electrostatic Desalting
c)	Atmospheric and Vacuum Fractionation	Atmospheric and Vacuum Fractionation	Atmospheric and Two Stage Vacuum Fractionation
d)	Thermal Cracking	Visbreaking	Visbreaking and Coking
e)	Catalytic Cracking -Houdriflow or Thermofor	Fluid Catalytic Cracking	Fluid Catalytic Cracking
f)	Catalytic Reforming - Platforming	Catalytic Reforming -Platforming	Catalytic Reforming - Powerforming
g)	Sulphuric Acid Polymerization	Hydrotreating - Unifining	Hydrotreating - Unifining
h)	Hydrofluoric Acid Alkylation	Phosphoric Acid Polymerisation	Hydrocracking - Isomax
i)	Solvent Refining (i) Sulphur Dioxide-Aromatics (ii) Furfural - Lube Oils	Sulphuric Acid Alkylation	Hydrogen Manufacture
j)	Lube Oil Dewaxing Pressing and Sweating	Solvent Refining (i) Udex-Aromatics (ii) Furfural - Lube Oils	Isomerisation
k)	Lube Oil Finishing -Percolation and Filtration	Lube Oil Solvent -Dewaxing	Aluminium Chloride Alkylation - DIP
1)	Wax Finishing	Wax Finishing	Solvent Refining (i) Sulfolane - Aromatics (ii) Furfural - Lube Oils

	Older Technology	Typical Technology	New Technology
m)	Grease Manufacture	Lube Oil Finishing - Continuous Contact Filter	Lube Oil Solvent Dewaxing
n)	Propane Deasphalting	Grease Manufacture	Wax Finishing Hydrotreating
o)	Drying and Sweetening (i) Girbotol (ii) Doctor Treating	Propane Deasphalting	Lube Oil Finishing -Hydrotreating
p)	Product Blending and Storage	Drying and Sweetening (i) Girbotol (ii) Copper Sweetening (iii) Various Caustic Treatments	Grease Manufacture
q)	--------------	Products Blending and Storage	Propane Deasphalting
r)	--------------	---------------	Drying and Sweetening (i) Girbotol (ii) Inhibitor Sweetening - Merox
s)	--------------	---------------	In-line Product Blending-Storage

It can be seen that this grading system applies principally to a large oil refinery - in fact the hypothetical basis for the system is a 100,000 bbl/day refinery. Consequently, the grading of the small Ontario refineries by this system is questionable. Nevertheless, the existence of production units which are predominantly new technology, typical technology or older technology in a small refinery justifies the placement of the refinery in the respective category. Thus, on this basis, the relative levels of technology of the seven Ontario oil refineries are as outlined in the following summary:

B.P. Canada Limited	- all units typical technology
Gulf Canada Limited	- Predominantly typical technology with some older technology units. Some units not classifiable by this system.
Imperial Oil	- Mainly typical technology with some elements of new and older technology. Many units not classifiable by this system.
Regent Refining Co. of Canada Limited	- Mainly typical technology.
Shell Canada Ltd. - Corunna	- Mainly typical technology.
Shell Canada Ltd. - Oakville	- Roughly and evenly distributed between new and typical technology. Some units not classifiable.
Sun Oil Company Ltd.	- Mainly typical technology.

It is evident that this classification system is not entirely satisfactory for the Ontario oil refineries because the dividing line between the three technology levels is somewhat obscure and because a number of refineries have multiple levels of technology.

The 1967 Domestic Refinery Effluent Profile by the American Petroleum Institute Committee on Air and Water Conservation adopted a classification system which is more reflective of the influence of oil processing complexity on overall waste load characteristics. The following categories were included in the effluent profile:

Category A - Crude Topping (Atmospheric and/or Vacuum Distillation)
Category B - Topping and Catalytic Cracking
Category C - Topping and Cracking plus Petrochemicals
Category D - Integrated (Topping, Catalytic Cracking and Lube Oil Processing)
Category E - Integrated plus Petrochemicals

No attempt was made to categorize the various product upgrading processes such as reforming, alkylation, hydrotreating, drying and sweetening because of the widespread use of these processes in conjunction with the fundamental processes already categorized. Similarly, the use of solvent refining and dewaxing are implied in lube oil processing while the manufacture of oil derived chemicals, including aromatics via solvent extraction (Udex - BTX), is included in categories C and E.

On this basis, the Ontario oil refineries may be classified as follows:

B.P. Canada Limited	- Category B
Gulf Canada Limited	- Category D
Imperial Oil Enterprises	- Category E
Regent Refining Canada Ltd.	- Category C
Shell Canada Ltd. - Corunna	- Category B
Shell Canada Ltd. - Oakville	- Category B
Sun Oil Canada Limited	- Category B

It can be seen that this classification system leaves two principal groups of refineries with Gulf Canada Limited and Imperial Oil Enterprises Limited in individual categories. If the petrochemical complex of Imperial Oil Enterprises Limited is disregarded, it is possible to place these latter two refineries in the same category. However, other factors mentioned at the beginning of this discussion, such as production volume, pollution control technology and refinery age may also be influential in the classification. Technology level is related to refinery age, although the need for refineries to continuously up-grade processing technology in order to remain competetive probably nullifies this relationship--vis. Imperial Oil Enterprises Limited which is the oldest Ontario oil refinery, yet is one of the most technologically advanced. Refinery size, ie. production volume, is an important factor and tends to follow the American Petroleum Institute oil processing complexity categories. (eg.)

Imperial Oil Enterprises Ltd.	100,000bbl/day	Category E
Gulf Canada Ltd.	61,500bbl/day	Category D
Shell Canada Ltd. - Corunna	45,000bbl/day	Category C
Regent Refining Canada Ltd.	47,000bbl/day	Category C
Shell Canada Ltd. - Oakville	38,000bbl/day	Category B
B.P. Canada Limited	35,000bbl/day	Category B
Sun Oil Company Limited	25,000bbl/day	Category B

The degree of pollution control technology in each of the refineries is difficult to assess, since the relative levels of technology of certain pollution control facilities are not clear, eg. deep well disposal and activated sludge, biological treatment of phenolic wastewaters achieve similar goals yet the relative technology level of each process is debatable. Suffice to say that the newer refineries such as B.P. Canada Limited and Shell Canada Limited in Oakville tend to be more advanced in terms of pollution control than the older refineries such as Gulf Canada Limited.

Taking all of these factors into consideration, it was decided that the Ontario oil refineries would be classified into three groups; namely, the older, larger, and more complex integrated refineries, Imperial Oil Enterprises, (excluding the chemical complex, plant #3) and Gulf Canada Limited, the older, medium sized and less complex refineries, Shell Canada Limited - Corunna and Regent Refining Canada Ltd; the newer, smaller and less complex refineries, B.P. Canada Limited, Shell Canada Limited - Oakville and Sun Oil Company Limited.

Effluent Waste Loadings

Table I on page 18 is a summary of the effluent waste loadings for the seven Ontario oil refineries grouped into the three classifications previously discussed. This table indicates how the refineries compare with each other, both overall and within the classification groups, in terms of general effluent quality.

As is to be expected, the larger, integrated and more complex refineries in Group 1 generally produce substantially greater waste loadings than the other refinery groups. However, a more meaningful comparison of this aspect of the situation is provided in Table II on page 22 where waste loading-production relations are summarized. This will be discussed more fully later.

It should be noted that the waste loadings in Table I are gross waste loadings and as such include the service water contribution. This can be a significant but variable factor at all of the refineries and particularly so in the Sarnia region. Unfortunately, samples of the service water were not taken at all of the refineries during the surveys in 1968. Consequently, a comparison on the basis of net waste loadings could not be made.

TABLE I

GROSS EFFLUENT WASTE LOADINGS

Refinery	Classification Group	Waste Flow mgd.	COD lbs/day	Ether Solubles lbs/day	Phenols lbs/day	Total Nitrogen lbs/day	Free Ammonia lbs/day
Gulf Canada Ltd.	I	43.6	15320	835	97.2**	1560	1125
Imperial Oil Enterprises Ltd*	I	48.4	22265	5545	73.4	485	120
Regent Refining Canada Ltd.	II	27.5	11000	0	11.3	12920	440
Shell Canada Ltd. - Corunna	II	44.2	15600	2000	31.0	13554	2000
Shell Canada Ltd. - Oakville	III	0.56	1352	72	0.6	1565	1150
Sun Oil Co. Ltd.	III	16.0	5730	583	11.0	229	94
B.P. Canada Ltd.	III	0.40	190	12	0.08	61	44
	Total	180.66	71457	9047	224.6	30374	4973

* Imperial Oil Enterprises Ltd loadings do not include loadings from the chemical complex, Plant #3.

** This value is untypical and has been greatly reduced since the completion of this report.

On the basis of the net waste loadings that are available from the 1968 survey data and company monthly analysis reports for the periods when the surveys were carried out at those refineries where no raw water sample was taken, it is concluded that the service water contribution to most of the waste loading data in Table I is not of major significance. Exceptions are the waste loadings for total nitrogen and COD which are influenced to varying degrees by the raw water contribution.

Certain of the wide differences in effluent quality between the various refineries are a function of the nature of the particular refinery. For example, the high ammonia waste loading from the Shell Canada Ltd. - Oakville refinery in relation to the other Group III refineries is believed to be attributable to the greater use of hydrogen treating in this refinery. This also applies to the high ammonia loading from the Shell Canada Ltd. - Corunna refinery. It can be seen that waste volumes from the Shell Canada Limited and B.P. Canada Ltd. refineries are considerably less than other refineries and this is because total recirculation of cooling waters is practiced at both these refineries. These two refineries also tend to be substantially lower in all other parameters and this is a function of the high level of waste treatment technology employed at these refineries and the fact that, because of the recirculation of cooling waters, the total waste flow is treated. Recirculation of cooling water at these two refineries has, therefore, been beneficial in terms of pollution control in reducing waste volumes to manageable proportions.

The Group I refineries, Gulf Canada Limited and Imperial Oil Enterprises Limited, account for 73% of the total phenolic and 70% of the total ether solubles waste loadings of the Ontario oil refining industry while being responsible for only 44% of the crude oil refining capacity.

Generally, waste loadings from the refineries in the Sarnia area are higher than those of the refineries in the western Lake Ontario region. This is largely a function of the different receiving stream conditions in Sarnia, which do not dictate the rigid adherence to OWRC effluent quality objectives that the relatively static conditions in Lake Ontario may require in order to prevent localized pollution and/or contamination of municipal water supplies.

In the Sarnia district, the OWRC regulatory program for the oil industry has taken the form of the use of OWRC effluent quality objectives as a target to be achieved, tempered by considerations of the effluent waste loadings in pounds per day and the estimated assimilative capacity of the receiving stream, the St. Clair River. In the western Lake Ontario region OWRC objectives have tended to be enforced as effluent quality limits because of the proximity of municipal water intakes and

because of the relatively static nature of the receiving watercourse and the consequent lack of meaningful estimates of assimilative capacity and susceptibility to localized pollution.

Waste Loadings and Production Relations

At the outset it must be recognized that the waste loading production relations of the wastewaters before treatment represents a much more valid comparison of waste production for the seven refineries in terms of efficiency of in-plant control of wastes and the waste producing potential of the various sizes and types of refinery. Unfortunately, insufficient data was collected during the 1968 surveys for such a comparison to be made. Therefore, the waste loading production relation data contained in Table II are a reflection of the degree and efficiency of effluent treatment practices within the Ontario oil refining industry as well as being to some degree related to the magnitude of primary waste production. It seems likely that the older more complex refineries which are evidently less efficient in effluent treatment are also the refineries which produce the greater magnitude of wastes to be treated per unit of production. It is on this basis that the discussion which follows is presented.

It can be seen from Table II on page 22 that effluent waste loadings per unit of production at the seven refineries correlate to some degree with the classification system. Higher loadings of phenols and ether solubles and higher waste volume per 1000 barrels of crude processed appear to be characteristic of the Group I refineries, while the higher loadings of total nitrogen and the median levels of phenols waste loadings per production unit are associated with the Group II refineries. The lower loadings in all parameters for the Oakville refineries of Shell Canada Limited and B.P. Canada Limited are to be expected to view of the high degree of wastewater re-use and waste treatment practiced at these refineries. It is, therefore, perhaps unreasonable to compare the remaining Group III refinery, that of Sun Oil Company Limited, with these two refineries since, although all three refineries have similar levels of production technology, the waste disposal and waste treatment procedures at the Sun Oil Company Limited refinery are markedly different from those of the other two refineries.

Similarly, the comparison between the two Group II refineries must be qualified by the fact that the Corunna refinery of Shell Canada Limited utilizes deep well disposal for wastewaters which, in the Regent Refining Company Limited refinery are treated biologically.

Nevertheless, in this instance, the net effect in terms of pollution control is almost the same and, therefore, the comparison is valid.

As mentioned previously, the relative waste loadings of certain parameters for many of these refineries are influenced by the nature of manufacturing operations in the refinery. It has been suggested, for example, that the ammonia waste loading is related to the amount of hydrogen treating carried out in the refinery. There is some verification of this in that ammonia waste loadings per 1000 barrels of crude throughput are higher for the Gulf Canada Limited and the two Shell Canada Limited refineries, where hydrogen treating is used to a significant degree. However, certain of the other refineries utilize hydrogen treating yet have no major ammonia waste loading. Also, the nature and extent of sour water stripping operations are likely to influence the ammonia waste loading since stripping under alkaline conditions would tend to remove ammonia. The degree to which ammonia is removed in sour water stripping is largely dependent upon the stripping medium, i.e. either steam or flue gas, and the temperature and residence time in the stripper. In general, the purpose of sour water stripping is to remove toxic sulphides from wastewaters prior to biological treatment. Ammonia may be removed by this pretreatment either incidental to this primary purpose of the process or by sizing and designing the stripper accordingly. Only one refinery, that of B.P. Canada Ltd., has stripping facilities which can be operated to remove ammonia as well as sulphides yet pH control problems have dictated that the facilities be operated to remove mainly sulphide.

As noted at the beginning of this discussion, the data in Table II are based on effluent characteristics after treatment so that the use of these data as a basis for an assessment of the effects of pretreatments such as sour water stripping is not valid. There are many factors which influence, to varying degrees, the relative levels of effluent waste loadings and production relations at all of the seven refineries. These may be summarized as follows:

1. crude oil characteristics,
2. production technology,
3. operating efficiency,
4. wastewater re-use,
5. wastewater segregation,
6. waste treatment technology,
7. waste treatment efficiency.

TABLE II

WASTE LOADINGS AND PRODUCTION RELATIONS

	CLASSIFICATION GROUP	PRODUCTION BBL/DAY	WASTE FLOW MGD/1000BBL	COD LBS/1000BBL	PHENOLS LBS/1000BBL	ETHER SOLUBLES LBS/1000BBL	TOTAL NITROGEN LBS/1000BBL	FREE AMMONIA LBS/1000BBL
GULF CANADA LIMITED	I	55,000	0.79	307	1.94	16.7	31.2	22.5
IMPERIAL OIL ENTERPRISES LTD.*	I	35,000	0.51	239	0.79	59.5	5.1	1.3
REGENT REFINING CANADA LTD.	II	46,500	0.58	236	0.24	0	278	9.5
SHELL CANADA LTD. – CORUNNA	II	45,000	0.38	347	0.69	44.5	302	44.5
SHELL CANADA LTD. – OAKVILLE	III	33,500	0.14	34.3	0.015	1.8	39.6	29.2
SUN OIL COMPANY LTD.	III	25,000	0.64	229	0.44	23.3	9.2	3.8
B. P. CANADA LTD.	III	34,000	0.12	5.6	0.002	0.3	1.8	1.3

*CHEMICAL COMPLEX, PLANT #3
WASTE LOADINGS EXCLUDED.

There are not sufficient data available to fully evaluate all of these factors, yet some general inferences can be drawn from the data that are available.

1) Variations in crude oil characteristics in the Ontario oil industry tend to be limited to the sulphur content, which influences the sulphide concentration in wastewaters such as desalter effluents and sour waters.

2) The influence of production technology on waste characteristics is difficult to define. It is evident from Table II that the effects of variation in production technology in the three classifications of Ontario oil refineries are accompanied by other fundamental differences in the refineries such as size, age, pollution control technology and complexity. It is known that certain processes are prime sources of specific waste constituents. For example, catalytic cracking units contribute in the order of 90% of the phenolic waste loading from a refinery. It is possible, therefore, that the proportion of crude throughput subjected to catalytic cracking is related to the phenolic waste loading. However, this does not appear to be the case. The proportion of crude throughput catalytically cracked is about the same for all of the Ontario refineries and does not reflect the wide variations in phenolic loadings per unit of crude throughput indicated in Table II . It is most likely that this variation is more indicative of the variation in the degree of efficiency of the re-use and control of phenolic wastewaters than in the primary production of phenols by catalytic cracking or other fundamental processes.

As has been noted previously, certain specific aspects of production technology, such as the degree of distillate hydrogen treating carried out in the refinery, may be influential in terms of specific waste characteristics (in the case of hydrogen treating the ammonia content). The effects of more subtle differences, such as those between two types of catalytic cracking units utilizing the same fundamental process, are difficult to determine without intensive in-plant sampling and analysis of wastewaters. There are references in the literature to variations in the yield of phenolics from different catalytic cracking process but these are associated with differences in fundamental processes, for example, between a conventional fluid catalytic cracking unit and a steam cracking unit.

3) Operating efficiency, both continuously and on a short term basis, is also a difficult factor to assess without an intimate knowledge of the industry generally, and the specific refinery under consideration. Intermittent losses of high strength wastes by accidental spills or plant upsets occur with sufficient frequency at certain refineries to give rise to doubts about the operating efficiency of these refineries. During the first six months of 1969, four significant spills of oil to the St. Clair River attri-

butable to the oil industry were reported, and numerous other minor spills occurred during the same period.

The 1968 survey data, on which this report is largely based, is qualified for all but two of the seven refineries by the fact that conditions were abnormal due to minor or major upsets in production or waste treatment units. Furthermore, stable conditions at the larger more complex refineries have seldom been encountered during previous OWRC surveys. These upset conditions do not always adversely affect effluent quality yet their frequency of occurrence emphasises the need for improved operating efficiency.

4) Wastewater re-use can obviously be a significant factor in the quantity and characteristics of refinery wastewaters prior to treatment. It has already been pointed out that cooling water re-use by the Shell Canada Limited - Oakville and B.P. Canada Limited refineries has reduced waste volumes to the point where the total waste flow can be treated. In-plant re-use of process wastewaters, such as the re-use of stripped foul condensates in crude oil desalters, can bring about significant reductions in the phenolic waste loadings from foul condensate systems since phenolics tend to be preferentially absorbed back into the crude oil (up to 75% of the phenolics in the foul condensates may be absorbed.) Some of these phenolics reappear in the crude unit foul condensate while the remainder is retained in the hydrocarbon streams and in some cases is subsequently rendered inactive by hydrogen treating processes. Quite dramatic reductions (up to two-thirds) in the total phenolic waste loadings were achieved at the Shell Canada Limited - Oakville refinery when this procedure was adopted. The degree to which phenolics, which are absorbed into the crude oil by recycling foul condensates through the crude oil desalters, subsequently re-appear in refinery wastewater may be related to the amount of hydrogen treating carried out in the refinery and the amount of steam stripping, or other sub-processes resulting in wastewaters, to which the crude oil fractions are subsequently subjected.

The Shell Canada Ltd. - Oakville refinery hydrogen treats a broad range of hydrocarbon fractions from the crude distillation unit and most of the phenolics present in the crude oil are likely to be associated with these fractions. Consequently, it has been suggested that the major reduction in phenolic waste loadings that resulted from the recycling of high phenolic foul condensates through the crude oil desalter was attributable to the subsequent hydrogen treating of the hydrocarbons fractions, which would tend to reduce or hydrogenate the phenolics absorbed by the crude oil from the foul condensate.

The only other refinery which practices re-use of foul condensates in this manner is the Corunna refinery of Shell Canada Ltd. Here, low phenolic foul condensates from the crude units are recycled through the crude oil desalters. There is not sufficient data to assess the overall effects of the procedure at this refinery other than to state that the phenolic loading of the crude units foul condensate is reduced from about 40 pounds per day to approximately 8 pounds per day (based on company estimates of the foul condensate volume and phenol concentrations and OWRC desalter effluent data).

It is probable that corrosion problems, both from the introduction of a high sulphur content stream (foul condensate) to the crude unit and the introduction of a high salt content desalter effluent to the sour water stripper, have discouraged other refineries from the re-use of foul condensates in crude oil desalters. In the case of the Corunna refinery of Shell Canada Ltd. no sour water stripping is carried out so the corrosion problem does not exist, while the Oakville refinery sour water stripper was constructed of corrosion resistant materials. A further objection to the re-use of foul condensates in crude desalters expressed by some refineries is that the reduced phenolic concentration may tend to upset subsequent biological treatment since the microorganisms have been acclimatized to phenolics as an essential food element and the reduction in the concentration of this food element adversely affects the microorganisms.

5) The degree of wastewater segregation into contaminated and non-contaminated streams practiced at the refinery may significantly influence effluent characteristics. Obviously, the untreated disposal of contaminated wastes in conjunction with clean water effluent is a prime example of this. Conversely, the disposal of large volumes of clean wastewaters to effluent treatment facilities will tend to reduce the efficiency of these facilities by absorbing hydraulic capacity. Furthermore, large volumes of cooling water in the wasteflow to oil-water separator systems tends to influence the distribution of dissolved organics such as phenols between the oil and water phases in favour of the water phase since, according to the distribution law, the ratio of the concentrations of phenols or dissolved organics in the oil phase and the aqueous phase should remain constant regardless of the amount of the dissolved substance.

6) The most significant difference in waste treatment and disposal practices in the Ontario oil refining industry occurs between those refineries which utilize deep well injection of high strength wastes and those refineries which practice biological treatment of these wastes. In the former case, the wastes in question are eliminated

from consideration as effluent waste streams to a natural watercourse whereas in the latter case, the treated effluent contributes to effluent waste loadings. Only one refinery, that of Shell Canada Limited in Corunna, practices deep well disposal as a complete alternative to biological treatment. Sun Oil Company Limited in Sarnia utilizes deep well injection for high phenolic waste streams, while streams such as crude unit foul condensates, which contain relatively low levels of phenolics, are biologically treated. The Imperial Oil Enterprises Limited refinery in Sarnia also practices deep well disposal but this is mainly for high strength wastes from the petrochemicals plant and has been largely disregarded in this report.

7) There are significant differences in the biological treatment processes employed at all of the Ontario oil refineries and in this respect, each refinery should be considered individually. There is insufficient data to carry out a detailed analysis of each biological treatment system. Table III on page 27 summarizes influent and effluent data for the six refinery biological treatment systems. It can be seen that most of the systems were operating efficiently with respect to the removal of phenolics when these data were collected. The degree of COD removal is variable from refinery to refinery whereas there appears to be some consistency in the efficiency of BOD removal. Nitrogen (largely in the form of free ammonia) does not appear to be removed very efficiently in these biological treatment systems and the removal that is achieved may be as much attributable to air stripping as to biochemical oxidation.

Comparisons with Data from the United States Oil Industry

In recent years, two major surveys of the status of water pollution control in the United States oil industry have been carried out, one, under the jurisdiction of the U.S. Department of the Interior, to provide cost estimates for the overall solution to water pollution problems (Cost of Clean Water Series) and the other, sponsored by the American Petroleum Institute, to obtain representative data on wastewater treatment and control practices. In both cases, the data were obtained from the responses to questionnaires sent out to the participating refineries. The data contained in both reports are comparable, but the American Petroleum Institute study is of more value in the comparison with the data from the Ontario industry since the waste loading-production relation data are based on effluent analysis for individual refineries, whereas the equivalent data in the U.S. Department of the Interior study are calculated waste loading-production relations for hypothetical 100,000 barrels per day refineries in the three technology levels considered.

TABLE III

ANALYTICAL DATA FOR REFINERY BIOLOGICAL TREATMENT SYSTEMS

REFINERY	CLASSIF'N GROUP	WASTE FLOW GPD	PHENOLS - PPB			COD - PPM			BOD - PPM			TOTAL KJELDAHL NITROGEN PPM		
			INFLUENT	EFFLUENT	% REMOVAL	INFLUENT	EFFLUENT	% REMOVAL	INFLUENT	EFFLUENT	% REMOVAL	INFLUENT	EFFLUENT	% REMOVAL
IMPERIAL OIL ENTERPRISES	I	300,000	>3000	>1200	---	1880	770	59	---	---	---	50	35	30
GULF CANADA LIMITED	I	162,000	220,000	126	99.9	870	233	73	425	140	67	330	240	30
REGENT REFINING CANADA LTD.	II	140,000	115,000	3250	97.0	725	650	10	420	188	61	280	240	14
B.P. CANADA LIMITED	III	400,000	425,000	55	99.9	138	23	83	146	6	96	17	14	18
SHELL CANADA LTD. OAKVILLE	III	576,000	9,000	105	99.9	565	242	57	253	89	65	253	257	0
SUN OIL CO. LIMITED	III	22,000	3,000	50	98.5	161	--	--	54	37	32	5	--	--

TABLE IV

COMPARISONS WITH UNITED STATES DATA*

WASTE LOADING PRODUCTION RELATIONS

REFINERY COMPLEXITY GROUP AND APPROPRIATE ONTARIO OIL REFINERY	COD LBS/1000BBL			OIL LBS/1000BBL			PHENOLS LBS/1000BBL		
	RANGE	MEAN	WEIGHTED AVERAGE	RANGE	MEAN	WEIGHTED AVERAGE	RANGE	MEAN	WEIGHTED AVERAGE
COMPLEXITY GROUP B - CRUDE DISTILLATION AND CRACKING PLANTS	6 - 600	95	78	<1 - 64	5	6	<0.1 - 8.6	1.0	< 1
B.P. CANADA LTD.		5.6			0.3			0.002	
SHELL CANADA LTD. - OAKVILLE		34.3			1.8			0.015	
SUN OIL CO. LIMITED		22.9			23.3			0.44	
COMPLEXITY GROUP C - CRUDE DISTILLATION AND CRACKING PLANTS PLUS PETROCHEMICALS	27 - 209	97	96	4 - 38	14	14	<0.01 - 7.0	1.8	2.0
REGENT REFINING CANADA LTD.		236			0			0.24	
SHELL CANADA LTD. - CORUNNA		347			44.5			0.69	
COMPLEXITY GROUP D - INTEGRATED REFINERY	26 - 649	168	159	<1 - 163	28	26	0.01 - 13.0	2.5	4
GULF CANADA LTD.		307			16.7			1.94	
IMPERIAL OIL ENTERPRISES		239			59.5			0.79	

*A.P.I. REFINERY EFFLUENT SURVEY 1967, TABLE X DATA FOR REFINERIES WITH BIOLOGICAL TREATMENT

Table IV on page 28 is a comparison of waste loading-production relations data from the A.P.I. study with equivalent data for the Ontario oil refineries.

It can be seen that the U.S. data are widely variable and, for the purposes of this discussion, only the mean and weighted average data have been considered in the comparison with the individual Ontario refineries. In general, it appears that phenolic waste loadings per unit of production are less for the Ontario refineries than their U.S. counterparts while ether solubles waste loadings appear to be higher than U.S. data except for the two Ontario refineries with cooling water recirculation systems, B.P. Canada Ltd., and Shell Canada Ltd. - Oakville.

Comparisons with other Industries

Other industries which generate wastes containing oils, phenolics, and other constituents common to oil refinery wastewater include steel and organic chemicals industries. Table V outlines approximate total waste loadings from these industries in Ontario and these are compared with the total waste loadings from the oil refining industry as shown in Table I.

TABLE V

Comparisons with other Industries

	Flow mgd.	BOD lbs/day	COD lbs/day	Total Nitrogen lbs/day	Ether Solubles lbs/day	Phenols lbs/day
Steel	500	80,000	--	60,000	66,000	7,000
Organic Chemicals	395	202,000	--	--	6,500	1,128
Oil Refining	181	--	71,500	30,400	9,000	225

It can be seen that the two industries considered are far more significant sources of oil and phenolics than the oil industry, while the steel industry is a source of substantially greater oil and phenolic loadings. In fact, one steel mill in Ontario discharges ten times the total phenolic waste loading and four times the oil waste loading of the whole Ontario oil refining industry.

Future Considerations

The growth of the Ontario oil refining industry is best illustrated by the following table obtained from a publication of the Federal Department of Energy, Mines and Resources; Petroleum Refineries in Canada.

Percentage Crude Oil Refining Capacity by Province for Selected Years

Province	1955	1960	1965	1966
Quebec	34	31	30	33
Ontario	24	27	30	29
British Columbia	11	10	9	9
Alberta	13	10	9	8
Saskatchewan	11	7	6	6
Nova Scotia	3	5	7	6
New Brunswick	--	5	4	4
Manitoba	5	4	4	4
Newfoundland	0	0	1	1
Northwest Territories	--	--	--	--

During the period covered in this table, daily crude oil processing in Canada increased from about 500,000 barrels per day to about 1,000,000 barrels per day. Although crude oil refining capacity and daily crude oil processing data are not identical, it is reasonably correct to infer from these data that Ontario crude oil processing has increased from about 125,000 barrels per day in 1955 to about 300,000 barrels per day in 1966. It is also reasonable to expect a similar, if not accelerated rate of growth in the Ontario industry in the next ten years. This will likely involve the expansion of existing refineries and where this is not possible, such as at the Regent Refining Company of Canada Limited refinery in Port Credit, the construction of new refineries. It is almost inevitable that this will lead to increased pollutional loadings from the expanded refineries unless pollution control and treatment efficiency are upgraded to accommodate the increased loadings.

On the basis of submissions received from all the refineries, in response to the 1968 survey reports, it appears that the Ontario oil industry as a whole is moving towards upgrading treatment efficiency and reducing effluent waste loadings.

The following table summarizes tentative proposals and firm commitments received from each of the refineries:

Improvement Programmes for the Ontario Oil Refineries

Name	Programme
B. P. Canada Limited	No major improvements at this refinery since waste characteristics are in compliance with OWRC objectives.
Gulf Canada Limited	Changes in piping and increased waste storage capacity in the foul condensate system as well as increased biological treatment capacity are expected to considerably reduce phenolic waste loading. Improved oil skimming devices on separators, upgraded waste segregation to isolate clean cooling waters from oily waters and new surface drainage collection systems are all under active consideration and are expected to bring about significant reductions in oil loadings.
Imperial Oil Enterprises Limited	A new gravity separator has been designed to supplement an existing unit which was found to be a prime source of excessive oil and phenolic waste loadings. Application for approval of this unit is expected in late 1969. The installation of rotary drum skimmers and other improvements in oil skimming on existing separator systems are expected to further improve the control of oil losses at this refinery. In-plant changes and modifications to the biological treatment facilities have also been implemented to reduce phenolic waste loadings. In conjunction with in-plant and effluent waste monitoring and sampling, it is expected that these changes will greatly reduce the incidences of uncontrollable spills and emergency discharges.

Regent Refining Company of Canada Limited	No major changes have been proposed at this refinery. The performance of the biological treatment unit is under investigation in an attempt to improve effluent quality in terms of phenols concentration.
Shell Canada Limited - Corunna	During 1968-69, additional brine handling facilities have been installed to store brine displaced from underground gas storage caverns. A new potentially oily water separator has also been put into operation and the existing unit will be used to treat surface drainage. Approval has been given for a secondary treatment system for oily water from the oily water separator by dissolved air flotation. Approval has been given for disposal facilities for cooling waters from the new catalytic reforming unit.
Shell Canada Limited - Oakville	No major improvements are planned at this refinery. Investigations into the performance of the biological treatment unit have been carried out to determine procedures to upgrade treatment efficiency and improve effluent quality.
Sun Oil Company Limited	No major improvements are planned since this refinery is in essential compliance with OWRC objectives.

Contingency planning to deal with oil spills is becoming of increasing concern to the Ontario oil industry. A cooperative approach has been developed in the western Lake Ontario region with the various refineries making available essential equipment such as control booms and boats in the event of a major spill at one of the participating refineries. Also, two of the refineries, namely Gulf Canada Ltd. and Shell Canada Ltd. are cooperating in the lease of a boat.

A similar approach is being formulated in the Sarnia area with the two major refineries, Imperial Oil Enterprises Limited and Shell Canada Limited having obtained the essential control equipment and dispersent chemicals while the other industries, including the chemicals and polymers manufacturers, in the area are considering participation in the cost and use of this equipment. At the present time, there is

no province-wide contingency plan to deal with a major spill. Numerous federal, provincial, state and international agencies concerned with the Great Lakes system are beginning to participate in the development of a plan for spills on the Great Lakes and it appears likely that any Ontario plan(s) will also deal with spills on inland waters.

Past experience, both in Ontario and overseas, indicates that there is a great need for improved techniques to deal with oil spills. Current knowledge on the subject suggests that the only practical and effective ways to deal with oil spills are via the use of sinking agents and/or dispersents (with varying levels of toxicity to aquatic organisms) or to await the arrival of the oil slick on shore and effect the cleanup there by the use of adsorbents such as straw or polyurethane foam. Oil control booms are generally ineffective in all but the most sheltered bodies of water and other control devices such as air bubble barriers, have not been shown to be any more efficient.

Future OWRC industrial pollution control programmes are likely to place more emphasis on the quality of receiving watercourses as it relates to industrial discharges. Policy guidelines issued in 1967 outlined the direction which future programmes would take with respect to overall water resource management in the province and, specifically, with respect to pollution control. Ultimately, this will involve management on a drainage basin or watershed basis. Various existing and potential uses of water in the drainage basin will be determined and quality criteria developed for these various uses. Based on these criteria, objectives and/or standards of receiving water quality will be established for the drainage basin and subsequently, effluent requirements or restrictions will be set at the discharge point to achieve or maintain the desired water quality. Thus, the assimilative capacity of the receiving watercourse will be taken into account in settling future effluent quality standards, but the principle is also established that all wastes prior to discharge to any watercourse should receive the best practicable treatment or control. This is considered essential if progress is to be made in pollution control to achieve a general improvement in water quality and consequently, a greater potential for more varied uses.

The complete economic analysis of a drainage basin with regard to water usage, both present and future, is a complex undertaking involving many factors. The application of this approach to waters such as the St. Clair River and Lake Ontario is further complicated by the size and nature of these waters. It is inevitable, therefore, that judgements will have to be made, as in the past, on the basis of information which is, at best, incomplete. Consultations with all parties having an interest in, or who will be affected by decisions pertaining to water resources management in a drainage basin will be an essential part of the decision making process.

TABLE VI

AROMATIC HYDROCARBONS FROM PETROLEUM REFINERY WASTES[a]
DECEMBER 16-18, 1967
JANUARY 15-16, 1968

No.	Location	Benzene	Toluene	Ethyl-Benzene	Xylene	Cumene	Mesitylene	P-Cymene	Total Aromatic
C1	Benzene sewer	6.20	1.40	-	-	-	-	-	7.60
C2	Dock	6.00	.13	-	-	.10	.04	-	6.27
C3	River	1.00	-	.02	-	.04	.05	-	1.11
C4	Pressure sewer	3.20	0.10	-	-	.009	.012	.01	3.33
A5	Contaminated sewer	8.70	0.25	5.00	-	-	-	-	13.95
A6	Processing sewer	25.00	2.50	0.25	0.70	1.25	0.52	-	30.22
A7	Outfall	60.60	-	-	-	0.75	0.45	-	61.80
B8	Oily Water separator	25.80	60.00	5.00	3.00	-	-	0.75	94.55
B9	Potentially oily sewer	251.00	-	-	-	-	-	-	251.00
B10	Outfall	4.20	3.20	0.05	0.25	-	-	-	7.70
B11	Aromatic unit	150.00	0.80	0.60	0.13	-	-	-	151.53
B12[b]	Aromatic unit	370.00	23.00	90.00	28.00	-	-	-	511.00
D13	Ditch (Hwy 40)	22.00	5.00	0.13	0.07	1.00	5.10	-	33.30
B14[c]	Outfall	25.10	1.10	-	1.50	-	-	-	27.70
B15[c]	Aromatic unit sewer	8.10	4.20	-	0.16	0.037	0.035	0.020	12.55
B16[c]	Potentially oily sewer	62.00	-	-	15.30	38.00	-	0.81	116.11
B17[c]	Oily water separator	75.00	4.40	0.20	-	0.40	0.05	-	80.05

a = all concentrations are expressed in parts per million
b = 113 ppm of styrene was found
c = B14 - 17 Samples taken when toluene unit was in operation

TABLE VII

COMPARISON OF PHENOLIC COMPOUNDS
FOUND BY G.C. AND BY CHEMICAL METHOD

No.	Phenol	O-cresol	P-cresol	O-ethyl Phenol	P-ethyl Phenol	2,3-xylenol	2,4-xylenol	3.4-xylenol	3,5-xylenol	Total phenol from G.C.	Total phenol found from chemical method
C1	142	--	40	--	--	--	--	--	--	182	120
C2	--	--	--	--	--	--	42	--	--	42	0
C3	--	--	--	--	--	--	--	--	--	0	0
C4	55	--	--	--	--	--	--	--	--	55	60
A5	172	--	--	--	--	40	--	--	--	212	120
A6	700	--	--	500	100	500	--	--	--	1,800	1,200
A7	8	--	--	--	--	--	--	--	--	8	8
B8	1,100	100	550	--	720	--	150	80	--	2,500	1,200
B9	925	--	150	--	640	125	--	100	--	1,740	1,200
B10	120	--	--	--	--	--	--	--	--	120	100
E11	--	140	--	--	--	--	--	--	--	140	150
E12	60	580	--	--	76	--	--	60	--	676	600
D13	--	--	--	--	--	--	--	--	--	0	120
B14	--	40	--	--	500	--	--	--	--	540	50
B15	80	--	--	260	--	--	--	--	--	340	300
B16	--	33	5	--	825	160	--	--	--	1,023	8
B17	--	--	--	--	--	--	--	--	--	0 --	800 --

All concentrations are expressed in ppb
See Table VI for identification of samples

The direct influence that these policies will have on the Ontario oil industry is to some degree a matter of conjecture. Based on the high standards of effluent quality that the industry now maintains, it appears likely, however, that the effects will be well within the capacity of the industry to deal with.

In terms of specific pollution parameters and associated considerations, advances in the technology of pollution control may dictate the removal from refinery effluents of waste constituents which are at present, not considered. With more sophisticated analytical techniques, the significance of phenolics in refinery effluent may be de-emphasized in favour of concern for more refractory and long lived taste and odour producing compounds such as naphthalene, ethyl-benzene and styrene. Also, the presence of a wide range of aromatic compounds, some of which are known to be toxic, in refinery effluent may be a cause for greater concern than at present. Tables V & VI on pages 29 and 34 indicates the results of gas chromatographic analysis of various wastewaters from a number of refineries in the Sarnia area for aromatics and phenolics respectively. It is evident from Table V that many refinery wastewaters are contaminated to a significant degree by aromatics, which would not be detected by the conventional ether solubles determination procedure. Effluent concentrations as high as 90 ppm aromatics (predominantly benzene) are indicative of wastewaters which would be significantly toxic to fish, while recommended maximum permissible concentrations of benzene in drinking waters range from 4.5 ppm to 0.5 ppm.

It can be seen from Table VI that these same wastewaters show consistently higher phenolics concentrations by the gas chromatographic technique than by the conventional chemical determination, the 4-Amino antypyrene method. In many cases, a significant portion of the phenolics present, are other than monohydric phenol. This may explain the higher yield from the gas chromatographic method of analysis, since the chemical analytical technique does not detect para-substituted phenols and the higher polyhydric phenols do not react to the 4-Amino antipyrene reagent in the same manner as monohydric phenol. It is clear that conventional analytical techniques are inadequate to fully evaluate parameters such as phenolics and aromatics.

CONCLUSIONS AND RECOMMENDATIONS

Pollution control in the oil refining industry is generally satisfactory and vastly superior to other industries which are sources of phenolic and oil bearing wastewaters, such as steel mills and organic

chemicals manufacturing. One Ontario steel mill, for example, discharges more than ten times the total phenolic waste loading of the Ontario oil industry and four times the ether solubles waste loading.

The total daily waste loadings for the Ontario oil refining industry in terms of phenolics, oil, COD and nitrogen are 224 lbs., 9047 lbs., 71457 lbs., and 30374 lbs respectively, in a total waste flow of 181 mgd. The larger, older and more complex refineries, the Group I refineries, account for 73% of the total phenolic waste loading and 70% of the total ether soluble waste loading of the Ontario oil refining industry while being responsible for only 44% of the crude oil refining capacity.

Individual refinery effluent characteristics are influenced by a number of variable factors. Perhaps the most significant of these being the degree of cooling water recirculation or separation from contaminated waste flows. In the former case, the effect is not so much a reduction in overall waste loadings as a reduction in waste volume to manageable proportions, such that the total waste flow can be efficiently treated in conveniently sized facilities. In the latter case, the removal of clean water from contaminated waste streams is beneficial in reducing contaminated waste volumes to manageable proportions and in reducing waste loadings of soluble organics such as phenols, due to the change in the distribution of soluble organics between the oil and water phases of the contaminated waste streams brought about by the reduction in the ratio of water to oil. Subsequent gravity separation of these contaminated wastes thus removes the soluble organics in conjunction with the oil.

Effluent waste loadings in terms of oil and phenolics as related to crude oil processed, vary between 0.002 and 1.94 lbs. phenols per thousand barrels of crude processed and 0 to 44.5 lbs. ether solubles per thousand barrels.

The Ontario industry is generally superior to the United States oil industry in terms of waste loadings per unit of production for comparable sized refineries. In common with the United States industry, waste loadings for the Ontario oil refineries tend to be higher for the larger more complex refineries.

In general, the pollution problems associated with the Ontario oil industry are mainly related to inadequate control of accidental losses of high strength wastes through treatment plant overloading due to plant upsets, poorly segregated waste streams and treatment plant overloading due to inadequately sized facilities in the older refineries. These problems have been identified in the individual refinery reports and drawn to the attention of management. In all cases, positive action is planned or has been implemented to deal with these situations.

Contingency planning, to deal with major oil spills is being developed, via a cooperative approach within the industry. Preliminary procedures are also being drawn up to deal with these occurrences on a province-wide basis, via cooperation between concerned federal, provincial and international agencies.

Ontario, and Canada generally, is not as well organized as United States federal and state agencies in this area.

The OWRC regulatory programme for the Ontario oil refining industry is largely based on the application of effluent quality objectives derived from quality controls developed in the late 1940's by the International Joint Commission to preserve international boundary water quality. IJC effluent quality objectives are set at that concentration which in the opinion of experts will probably maintain receiving water quality at the desired level. Thus, for example, it is stated that 0.3 ppm iron will probably be maintained in a receiving water if effluent concentrations are maintained at less than 17 ppm; however, the scientific basis for this assumption is unknown.

The parameters used to describe the effluent characteristics of the oil refining industry in Ontario are inadequate and fail to identify and measure all of the potential contaminants of a refinery wastewater on a receiving stream. Phenolics analyses, both by the Gibbs procedure and the 4-Amino antipyrene method do not determine all phenolic compounds and the parameter itself is of doubtful value in its relationship to potential taste and odour problems in the receiving stream. There are numerous other compounds present in refinery wastewaters which impart objectionable tastes and odours to water and some of these undergo biochemical degradation at a slow rate (organic refractories) and as such, their effects on the receiving stream are likely to be prolonged.

Other compounds present in refinery wastewaters, particularly dissolved hydrocarbons, may exert acute or chronic toxic effects on organisms in the receiving stream. In this category are compounds such as benzene and its homologues.

Data collected during the individual refinery surveys were, in almost all cases, inadequate to provide detailed information on in-plant unit process waste loadings. Principle sources of the major waste parameters were indentified at each of the refineries but due to lack of flow information, sample points and waste characteristics generally, it was not possible to calculate waste loadings from these sources or loadings per unit of production.

In the light of the foregoing conclusions, the following recommendations are presented:

1. The future OWRC regulatory programme for the oil industry in Ontario place less emphasis on adherence to effluent quality objectives and more emphasis on waste loadings and receiving water quality characteristics.

2. Parameters other than non-volatile ether solubles and phenolics, as determined by the Gibbs or 4-Amino antipyrene methods, be developed to more adequately characterize refinery effluents in relation to their potential adverse effects on receiving waters. In this regard, parameters worthy of further consideration are volatile and non-volatile ether solubles, phenolics as determined by ultra violet and/or infrared spectroscopy or gas chromatography, neutral carbon chloroform extract and attendant threshold odour concentration, total organic carbon and bioassays involving fish toxicity studies.

3. Baseline biological and chemical characteristics of waters receiving, or which may receive, refinery effluents be determined in order to assess long term changes in these characteristics brought about by refinery waste disposal.

4. Multiagency contingency planning to deal with oil spills on the Great Lakes, be actively promoted by the OWRC as well as the organization of provincial manpower and resources to deal with spills on inland waters.

5. The Ontario oil industry intensify its efforts to control and deal with process upsets and other sources of inadvertent losses of oils and other high strength wastes. The cooperative approach towards oil spill contingency planning should be emphasized both in relation to emergency action and to the development of effective techniques to deal with oil spill cleanup.

6. Research programmes be undertaken by the oil industry and/or the OWRC to develop and evaluate dispersants, sinking agents and any other chemical or physical control devices applicable to oil spill control and cleanup.

APPENDIX I

Bibliography

1. Aqueous Wastes from Petroleum and Petrochemical Plants, by Milton R. Beychok

2. American Petroleum Institute Manual on The Disposal of Refinery Wastewaters - sixth edition and supplements.

3. Air and Water Conservation Expenditures of the Petroleum Industry in the United States, by Crossley, S-D Surveys Inc., sponsored by the American Petroleum Institute.

4. The Behaviour of Oil Water Mixtures in Separators, University of Wisconsin research report, sponsored by the American Petroleum Institute

5. Behaviour of Organic Chemicals in The Aquatic Environment, A literature Critique, research report of the Environmental and Sanitary Engineering Laboratories of Washington University, St. Louis.

6. The Cost of Clean Water, Volume III, Industrial Waste Profiles, No. 5, Petroleum Refining, by U.S. Department of the Interior F.W.P.C.A.

7. Oil Spillage Study Literature Search and Critical Evaluation for Selection of Promising Techniques to Control and Prevent Damage, Battelle Memorial Institute, Richland, Washington.

8. The Petroleum Handbook, staff publication of the Royal Dutch/ Shell Group of Companies.

9. Water Quality Criteria, State Water Quality Control Board Sacramento, California.

10. The Santa Barbara Channel Oil Spill, Report on a visit to Santa Barbara, California Feb., 11, 12th and 13th 1969, by F Boyce, Canada Centre for Inland Waters, Federal Department of Energy, Mines and Resources.

11. Standard Methods for the Examination of Water and Wastewater, 12th edition American Public Health Association.

12. Report to the Inter-Connecting Channels Advisory Boards on Water Pollution International Joint Commission, Summary of Waste Spills, - August, 1969.

Appendix (cont'd)

13. History of Lambton County by Victor Lauriston.

14. Petroleum Refineries in Canada, 1967 - Dept. of Energy, Mines and Resources, Ottawa 1.